

# Impacts of CaO solid particles in carbon dioxide absorption process from ship emission with NaOH solution

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**Abstract:** CO<sub>2</sub> emitted from ship exhaust is one of the major sources of atmospheric pollution. In order to reduce ship CO<sub>2</sub> emissions, this paper comes up with the idea of recovering CO<sub>2</sub> from ship exhaust by NaOH solution and improves the absorption rate by adding CaO solid particles. The effect mechanism of CaO solid particles on CO<sub>2</sub> absorption efficiency is analyzed in detail, and the mathematical model is deduced and the CaO enhancement factor is calculated through experiments. Experiment result demonstrates that the effect of CaO solid particles on the absorption of CO<sub>2</sub> in alkali solution is significant. The absorption rate of pure CO<sub>2</sub> gas, the simulated ship exhaust gas and 6135AZG marine diesel engine emission can be increased by 10%, 15.85% and 10.30%, respectively. So it can be seen that CaO solid particles play an important role in improving the absorption efficiency of ship CO<sub>2</sub> emission.

**Key words:** environmental protection, diesel emissions, CO<sub>2</sub> absorption, CaO particulate matter, enhancement factor

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## 0 Introduction

With the rapid development of the shipping industry, air pollution caused by marine diesel engine emissions draws more attention. The ship is a major means of transportation, producing a large quantity of CO<sub>2</sub> emissions<sup>[1]</sup>. The International Convention for the Prevention of Pollution from Ships of 1973, as amended by the Protocol of 1978, adopted by the IMO Marine Environment Protection Committee (MEPC) at its 62nd meeting in July 2011, approved the Energy Efficiency Design (EEDI), Ship Energy Efficiency Management Plan (SEEMP) and other ship energy efficiency standards. According to the tacit acceptance procedure, the amendment was enforced in 2015<sup>[2]</sup>, imposing severe restrictions on ship CO<sub>2</sub> emissions.

As the in-depth research on the effect of particulate matters on gas-liquid mass transfer, the concept of "enhancement factor" becomes popular, and the ratio of mass transfer rate between gas and liquid has been accepted<sup>[3]</sup>. Eq. (1) shows the definition of "enhancement factor".

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$$A = \frac{J_{\text{act}}}{J_{\text{out}}}, \quad (1)$$

where  $A$ ,  $J_{\text{act}}$  and  $J_{\text{out}}$  are manoeuvring indices;  $A$  is the total enhancement factor;  $J_{\text{act}}$  is the mass transfer rate with the solid particles;  $J_{\text{out}}$  is the mass transfer rate without solid particles. Eq. (1) demonstrates the effect of particulate matters on gas-liquid two-phase mass transfer, which is much closer to the actual situation.

It was found that when adding slight solid particles into the gas-liquid reaction, the mass transfer efficiency could be improved significantly. After investigating the zero-order and first-order reaction processes of the vapor phase on catalyst surface in a stirred tank, Yuan et al.<sup>[4]</sup> and Gutierrez et al.<sup>[5]</sup> concluded that the stirring rate, gas feed rate, catalyst particle concentration, particle size and other elements could affect the enhancement factor directly. Wimmers et al.<sup>[6]</sup> believed that there was a membrane at the gas interface in the activated carbon slurry and the solids concentration within the membrane area was much higher than that of the liquid phase. Liu et al.<sup>[7-9]</sup> carried out the experiment that  $\text{CO}_2$  was absorbed by ethanolamine solution within filler absorption tower and the absorption rate could be improved by increasing alkali concentration or circulating fluid flow. Excessive chemicals will be consumed by purely increase the alkali concentration, and by just increasing the circulating fluid flow also led to higher energy consumption, neither economic nor environmental friendly. In this paper, we come up with the idea that by adding solid particles into the alkaline liquor to improve  $\text{CO}_2$  absorption efficiency in both chemical and physical aspects, reducing chemicals and energy consumption.

In this paper, a certain amount of  $\text{CaO}$  solid particles is added into the  $\text{NaOH}$  solution to increase the  $\text{CO}_2$  absorption rate. The enhancement mechanism of solid particles in the alkali decarburization is investigated, which provides the theoretical and experimental basis for improving solid particles decarburization.

## 1 Solid Particles Mass Transfer Mechanism

According to the current researches, scholars did not draw a unified conclusion about solid particles function mechanism in gas-liquid mass transfer, as the results from experiments were not quite the same. Below are some major theories about solid particles mass transfer mechanism:

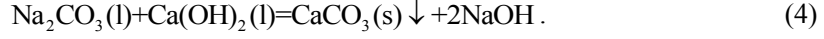
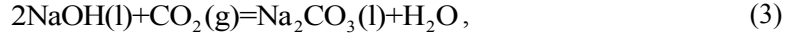
① particles have only physical absorption on gases component in the gas-liquid mass transfer area; ② particles catalyze in the chemical reactions involved in gas component; ③ particles react with gases to be transferred; ④ particles react with gases after getting dissolved in the gas-liquid mass transfer area; ⑤ particles work as the combinations of above four cases. This paper emphasizes on the mechanisms research synthesized ① and ④ theories.

### 1.1 Marine Alkaline Liquor Decarburization Mechanism

When adding  $\text{CaO}$  into the alkaline decarburization solution,  $\text{Ca(OH)}_2$  will be generated immediately after  $\text{CaO}$  solid particles react with water. The reaction equation is shown in Eq. (2).



After introduced into the alkaline solution,  $\text{CO}_2$  gas will react with  $\text{NaOH}$  and  $\text{Ca(OH)}_2$  solution. The reaction equation are



That is,  $2\text{NaOH(l)} + \text{CaO(s)} + \text{CO}_2(\text{g}) = \text{CaCO}_3(\text{s}) \downarrow + 2\text{NaOH(l)}$ .

From Eq. (4),  $\text{NaOH}$  can be regenerated and  $\text{NaOH}$  solution will be recycled, while  $\text{CaCO}_3$  is precipitated at the same time. Since the molecular weight of  $\text{Ca(OH)}_2$  is 74 and  $\text{CaCO}_3$  is 100, the total amount of solid particles is almost constant throughout the experimental cycle.

## 1.2 CaO Particles Enhanced Mechanism

The  $\text{CO}_2$  absorption by  $\text{NaOH}$  solution with  $\text{CaO}$  solid particles is a mass transfer process accompanied with chemical reaction, both the chemical reaction mass transfer enhancement and physical enhanced particulate matter mass transfer happen during the reaction period.

**1.2.1 Chemical enhancement mechanism** Eqs. (5) and (6) show the kinetic model of liquid membrane reaction and diffusion<sup>[10-11]</sup> in the reaction  $\text{CO}_2(\text{g}) + \text{Ca(OH)}_2(\text{l}) \xrightarrow{k_2} \text{CaCO}_3(\text{s}) \downarrow + \text{H}_2\text{O}$ .

The second order linear models are

$$\frac{d^2 c_{\text{CO}_2}}{dx^2} = \frac{k_2 c_{\text{CO}_2} c_{\text{Ca(OH)}_2}}{D_{\text{CO}_2, \text{L}}}, \quad (5)$$

$$\frac{d^2 c_{\text{Ca(OH)}_2}}{dx^2} = \frac{k_2 c_{\text{CO}_2} c_{\text{Ca(OH)}_2}}{D_{\text{Ca(OH)}_2, \text{L}}}, \quad (6)$$

where,  $c_{\text{CO}_2}$ ,  $c_{\text{Ca(OH)}_2}$ ,  $D_{\text{CO}_2, \text{L}}$ ,  $k_2$  and  $D_{\text{Ca(OH)}_2, \text{L}}$  are manoeuvring indices;  $c_{\text{CO}_2}$  is the concentration of  $\text{CO}_2$  at the interface,  $\text{kmol/m}^3$ ;  $c_{\text{Ca(OH)}_2}$  is the concentration of  $\text{Ca(OH)}_2$  at the interface,  $\text{kmol/m}^3$ ;  $D_{\text{CO}_2, \text{L}}$  is the diffusion coefficient of  $\text{CO}_2$  in liquid phase,  $\text{m}^2/\text{s}$ ;  $k_2$  is a reaction constant for the second stage,  $\text{m}^3/(\text{kmol} \cdot \text{s})$ ;  $D_{\text{Ca(OH)}_2, \text{L}}$  is the diffusion coefficient of  $\text{Ca(OH)}_2$  in liquid phase,  $\text{m}^2/\text{s}$ . When  $x = 0$ ,  $c_{\text{CO}_2} = c_{\text{CO}_2, \text{i}}$  ( $c_{\text{CO}_2, \text{i}}$  represents  $\text{CO}_2$  concentration,  $\text{kmol/m}^3$ ),  $\frac{dc_{\text{Ca(OH)}_2}}{dx} = 0$ ; when  $x = \delta$ ,  $c_{\text{Ca(OH)}_2} = c_{\text{Ca(OH)}_2, \text{L}}$ , where  $\delta$  is the film thickness of reaction,  $\text{m}$ .

Since the  $\text{Ca(OH)}_2$  concentration is almost constant during the reaction and involatile, therefore, the chemical enhancement factor can be expressed as below<sup>[12-13]</sup>.

$$E = \frac{\sqrt{D_{\text{CO}_2, \text{L}} k_2 c_{\text{Ca(OH)}_2, \text{i}}}}{k_{\text{L}}^0} \left/ \tanh \left( \frac{\sqrt{D_{\text{CO}_2, \text{L}} k_2 c_{\text{Ca(OH)}_2, \text{i}}}}{k_{\text{L}}} \right) \right., \quad (7)$$

where  $E$ ,  $c_{\text{Ca(OH)}_2,i}$ ,  $k_L^0$  and  $k_L$  are manoeuvring indices;  $E$  is chemical enhancement factor;  $c_{\text{Ca(OH)}_2,i}$  is concentration of  $\text{Ca(OH)}_2$  during the reaction period,  $\text{kmol/m}^3$ ;  $k_L^0$  is liquid phase mass transfer coefficient without chemical reaction,  $\text{kmol}/(\text{m}^2 \cdot \text{s} \cdot \text{kPa})$ ;  $k_L$  is liquid phase mass transfer coefficient with chemical reaction,  $\text{kmol}/(\text{m}^2 \cdot \text{s} \cdot \text{kPa})$ . Then the boundary conditions and integrate are brought into by combing Eqs. (5) and (6).

Then, the function model is

$$(E-1)D_{\text{CO}_2,L}c_{\text{CO}_2,i} = \frac{D_{\text{Ca(OH)}_2,L}}{v}(c_{\text{Ca(OH)}_2,L} - c_{\text{Ca(OH)}_2,i}), \quad (8)$$

Finally, the function model is

$$E = \frac{D_{\text{Ca(OH)}_2,L}(c_{\text{Ca(OH)}_2,L} - c_{\text{Ca(OH)}_2,i})}{vD_{\text{CO}_2,L}c_{\text{CO}_2,i}} + 1, \quad (9)$$

where  $v$  and  $c_{\text{Ca(OH)}_2,L}$  are manoeuvring indices;  $v$  is the velocity of  $\text{CO}_2$  in the solution,  $\text{m/s}$ ;  $c_{\text{Ca(OH)}_2,L}$  is concentration of  $\text{Ca(OH)}_2$  solution,  $\text{kmol/m}^3$ ;  
 $-D_{\text{CO}_2,L} \frac{dc_{\text{CO}_2}}{dx} = (1-\delta)k_2c_{\text{CO}_2,L}c_{\text{Ca(OH)}_2,L}$ .

**1.2.2 Physical enhancement mechanism** The physical enhancement is mainly about the mass transfer between gas and liquid. According to the dual-membrane theory<sup>[14-15]</sup>, it is necessary to meet the equilibrium state of the  $A$  component at the gas-liquid interface, i.e.,  $C_{A,i} = Hp_{A,i}$ . Where  $C_{A,i}$  is  $A$  component concentration in solution,  $\text{kmol/m}^3$ ;  $H$  is  $A$  component Henry coefficient,  $\text{m}^3 \cdot \text{kPa/kmol}$ ;  $p_{A,i}$  is  $A$  component partial pressure in gas phase,  $\text{kPa}$ . Since this study satisfies this condition, so the rate equation of  $\text{CO}_2$  diffused from the gas phase to the gas-liquid interface can be expressed below.

The first order linear model is

$$-\frac{dn_{\text{CO}_2}}{dt} = \frac{D_{\text{CO}_2,G}}{\delta_G}(p_{\text{CO}_2,G} - p_{\text{CO}_2,i})S, \quad (10)$$

where  $D_{\text{CO}_2,G}$ ,  $\delta_G$ ,  $p_{\text{CO}_2,G}$ ,  $p_{\text{CO}_2,i}$  and  $S$  are manoeuvring indices;  $D_{\text{CO}_2,G}$  is the diffusion coefficient of  $\text{Ca(OH)}_2$  in gas phase,  $\text{m}^2/\text{s}$ ;  $\delta_G$  is film thickness of  $\text{CO}_2$  in solution,  $\text{m}$ ;  $p_{\text{CO}_2,G}$  is the pressure of  $\text{CO}_2$  in solution,  $\text{kPa}$ ;  $p_{\text{CO}_2,i}$  is the pressure of  $\text{CO}_2$  during the reaction period,  $\text{kPa}$ ;  $S$  is the solubility,  $\text{g}$ .

The rate equation of the diffusion of  $\text{CO}_2$  components from the gas-liquid interface to the liquid phase is below.

The first order linear model is

$$-\frac{dn_{\text{CO}_2}}{dt} = \frac{D_{\text{CO}_2,\text{L}}}{\delta_{\text{L}}}(c_{\text{CO}_2,\text{i}} - c_{\text{CO}_2,\text{L}})S, \quad (11)$$

where  $\delta_{\text{L}}$  is film thickness of liquid reaction, m.

Combined with the definition of membrane transfer coefficient  $k_{\text{CO}_2,\text{G}} = \frac{D_{\text{CO}_2,\text{G}}}{\delta_{\text{G}}}$ ,  $k_{\text{CO}_2,\text{L}} = \frac{D_{\text{CO}_2,\text{L}}}{\delta_{\text{L}}}$ . The first order linear model is

$$N_{\text{CO}_2} = K_{\text{CO}_2,\text{G}}(p_{\text{CO}_2,\text{G}} - p_{\text{CO}_2}^*) = K_{\text{CO}_2,\text{L}}(c_{\text{CO}_2}^* - c_{\text{CO}_2,\text{L}}), \quad (12)$$

where  $N_{\text{CO}_2}$ ,  $k_{\text{CO}_2,\text{G}}$ ,  $p_{\text{CO}_2}^*$ ,  $k_{\text{CO}_2,\text{L}}$ ,  $c_{\text{CO}_2}^*$  and  $c_{\text{CO}_2,\text{L}}$  are manoeuvring indices;  $N_{\text{CO}_2}$  is physical enhancement factor;  $k_{\text{CO}_2,\text{G}}$  is gas phase mass transfer coefficient of  $\text{CO}_2$ ,  $\text{kmol}/(\text{m}^2 \cdot \text{s} \cdot \text{kPa})$ ;  $p_{\text{CO}_2}^*$  is the equilibrium pressure of  $\text{CO}_2$  in solution,  $\text{kPa}$ ;  $k_{\text{CO}_2,\text{L}}$  is liquid phase mass transfer coefficient of  $\text{CO}_2$ ,  $\text{kmol}/(\text{m}^2 \cdot \text{s} \cdot \text{kPa})$ ;  $c_{\text{CO}_2}^*$  is the equilibrium concentration of  $\text{CO}_2$  in solution,  $\text{kmol}/\text{m}^3$ ;  $c_{\text{CO}_2,\text{L}}$  is concentration of  $\text{CO}_2$  in solution,  $\text{kmol}/\text{m}^3$ ;

$$K_{\text{CO}_2,\text{G}} = \frac{1}{\frac{1}{k_{\text{CO}_2,\text{G}}} + \frac{1}{Hk_{\text{CO}_2,\text{L}}}}; \quad K_{\text{CO}_2,\text{L}} = \frac{1}{\frac{H}{k_{\text{CO}_2,\text{G}}} + \frac{1}{k_{\text{CO}_2,\text{L}}}}.$$

The total mass transfer resistance during the reaction process is the sum of the mass transfer resistance and the mass transfer resistance of the liquid phase<sup>[16]</sup>. The total mass transfer rate is the ratio of the total mass transfer ( $y - y^*$ ) to the total mass transfer resistance ( $1/K_y$ ), and regarding dilution solution, the equilibrium relationship between the dilute solution and the system is subject to Henry's law<sup>[17]</sup>  $y^* = mx$ , where  $y$  is molar concentration ratio of the gas phase;  $y^*$  molar concentration ratio of the gas phase balanced with it' s of the liquid phase;  $m$  is equilibrium constant;  $x$  is molar concentration ratio of the liquid phase;  $K_y$  is total mass transfer coefficient driven by  $(y - y^*)$ ,  $\text{kmol}/(\text{m}^2 \cdot \text{s} \cdot \text{kPa})$ .

$$\text{From the gas phase: } \frac{N_{\text{CO}_2}}{k_y} = (y - y_i) \text{ and liquid phase: } \frac{N_{\text{CO}_2}m}{k_x} = (y_i - y^*), \text{ where } k_y$$

is mass transfer coefficient of the gas phase,  $\text{kmol}/(\text{m}^2 \cdot \text{s} \cdot \text{kPa})$ ;  $k_x$  is mass transfer coefficient of the liquid phase,  $\text{kmol}/(\text{m}^2 \cdot \text{s} \cdot \text{kPa})$ ;  $y_i$  is molar concentration ratio of the gas phase during the reaction period; So we can conclude the result in Eq. (13)

$$N_{\text{CO}_2} = \frac{(y - y_i) + (y_i - y^*)}{\frac{1}{k_y} + \frac{m}{k_x}} = \frac{y - y^*}{\frac{1}{k_y} + \frac{m}{k_x}}. \quad (13)$$

From the differ phase:  $N_{\text{CO}_2} = \frac{y - y^*}{1/K_y} = K_y (y - y^*)$  and by comparison:  $\frac{1}{K_y} = \frac{1}{k_y} + \frac{m}{k_x}$ ,

the total mass transfer rate equation is calculated in terms of gas phase<sup>[18]</sup>, so the physical enhancement factor can be expressed.

The function model is

$$N_{\text{CO}_2} = \left( \frac{1}{\frac{1}{Hk_{\text{CO}_2, \text{L}}} + \frac{1}{k_{\text{CO}_2, \text{G}}}} \right) (p_{\text{CO}_2, \text{G}} - p_{\text{CO}_2}^*). \quad (14)$$

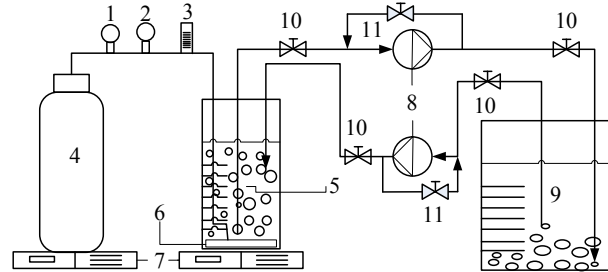
Therefore, the total enhancement factor of CaO particles is the sum of the chemical enhancement factor, Eq. (9), and the physical enhancement factor, Eq. (14).

Finally, the function model is

$$A = E + N_{\text{CO}_2}. \quad (15)$$

## 2 Experimental Condition

The main purpose of this experiment is to study the effect of solid particles on marine alkaline liquor decarburization; Figure 1 shows the experimental process.



1- Reducing valve, 2-Pressure gauge, 3-Flowmeter, 4-CO<sub>2</sub> cylinder, 5-Reactor, 6-Diffuser, 7-High-precision scale, 8-Gear pump, 9-Reservoir, 10-Regulate valve, 11-Bypass valve

Fig. 1 Facilities for marine alkaline liquor decarburization

As shown in Fig. 1, gas stored in the cylinder (CO<sub>2</sub> or ship simulated gas) is decompressed by reducing valve and regulated to the pressure that slightly higher than atmospheric pressure (0.103 MPa), then adjusted to an appropriate flow rate through flow meter 3, finally entered into the reactor 5 through the diffuser 6. In order to achieve a better absorption effect, it is necessary to limit the size of air bubble before entering the solution. High-precision scale 7 on the bottom is applied to measure the mass reduction of cylinder 4 and mass increment of reactor 5. Gear pump 8 keeps the whole system circulated. The diameter of the reaction vessel is 120 mm; solution's height is 240 mm; and the weight is 3 kg; the initial reaction temperature is 25 °C; diffuser's diameter is 104 mm; gas flow rate is 1 L/min; the experiment lasts 30 min; sample is took every 2 min.

## 2.1 Gas Used for the Experiment

The experiment uses three kinds of gas, namely pure CO<sub>2</sub>, simulated exhaust and diesel engine exhaust. The pure CO<sub>2</sub> is 99% purity gas produced by Shanghai Special Gas Co., Ltd. The simulated exhaust gas is applied in the experiment which is based on the exhaust gas data from 6S35 ME-B produced by MAN B&W Company. The diesel engine exhaust comes from MAN Shanghai Diesel Engine Co., Ltd and the simulating exhaust gas consists of N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and SO<sub>2</sub> with the mass fraction of 80.09%, 15.18%, 4.69% and 0.04%, respectively.

## 2.2 Experimental Chemicals

During the study, NaOH solid and CaO solid are used, the specific parameters are shown in Table 1.

Table1 NaOH solid and CaO solid specific parameters					
Solid NaOH (flake )			Calcium oxide (CaO particles)		
Charity test	Qualified	AL	≤0.00 2%	Cl	≤0.01%
Total nitrogen(N)	≤0.00 1%	K	≤0.05%	Sulfate (SO <sub>4</sub> )	≤0.1%
Chloride (Cl)	≤0.00 5%	Ca	≤0.01%	Loss on ignition	≤2.0%
Sulfate (SO <sub>x</sub> )	≤0.00 5%	Fe	≤0.00 1%	Fe	≤0.01 5%
Phosphate (PO <sub>x</sub> )	≤0.00 1%	Carbonate (Na <sub>2</sub> CO <sub>3</sub> )	≤1.5%	Alkali and magnesium	≤0.5%
Heavy metal (Pb)	≤0.00 3%	Content (NaOH)	≥96%	Heavy metal (Pb)	≤0.00 5%
				Acetic acid insoluble matter	≤0.05%
				CaO content	≥98.0%
				Particles volume	≤0.3mm

## 2.3 Measuring Instrument

Measuring instruments include 2 pieces of high-precision ACS-258 electronic scales, 1 piece of JJ324BC balance and 1 piece of MP512-02 pH meter. The maximum range and accuracy of the high-precision electronic scales are 15 kg and 0.1 g, similarly the pH meter is 14.00 pH and ± 0.002.

# 3 Experimental Results and Analysis

In order to analyze the effect of solid particles on CO<sub>2</sub> absorption, pure CO<sub>2</sub> gas is first introduced to NaOH solution, then to the mixed NaOH solution with CaO particles, finally the simulated ship exhaust gas is used for verification. CO<sub>2</sub> absorbance rate is the ratio of the mass of absorbed CO<sub>2</sub> to the total mass of CO<sub>2</sub> that enters the liquid, expressed as a percentage.

## 3.1 Study on CaO Enhancement Factor

In order to investigate the enhancement factor of CaO solid particles, 2.5 g, 1.25 g, 0.75 g, 0.375 g, 0.187 5 g and 0.093 8 g of CaO solid particles are used for the test respectively. It is found that when the mass of CaO exceeds 2.5 g, a large amount of Ca(OH)<sub>2</sub> particles will precipitate and obstruct the gas release, which is disadvantageous to CO<sub>2</sub> absorption. Therefore, this experiment takes the weight of 2.5 g as maximum, and halves the weight successively to explore the enhancement functions of CaO. Figure 2 shows the experimental results.

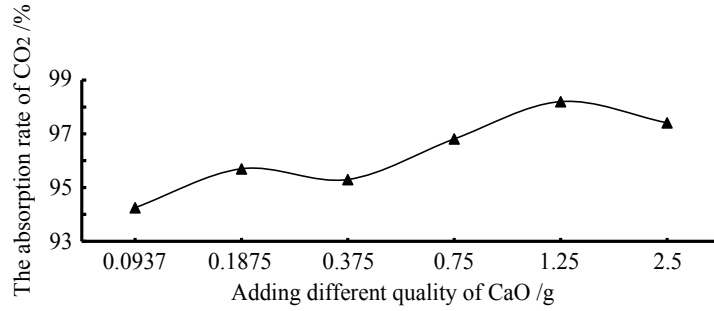


Fig. 2 CO<sub>2</sub> absorption rate varies with CaO weight

It can be seen from Fig. 2 that the average CO<sub>2</sub> absorption rate is 94.25% with 0.093 7 g CaO. As CaO increases continuously, the absorption rate also increases, indicating that the more particles, the more favorable of gas-liquid mass transfer. However, the average CO<sub>2</sub> absorption rate reaches the maximum value of 98.2% when CaO's weight reaches to 1.25 g. After increasing the weight of CaO to 2.5 g, the absorption rate slightly decreases to 97.41%, which means that CaO solid particles does improve the CO<sub>2</sub> absorption within a certain limit. When the mole ratio of NaOH to CaO is 135, the absorption of CO<sub>2</sub> in NaOH solution reaches the maximum, and the enhancement factor  $A$  is 1.1.

Through observation, Ca(OH)<sub>2</sub> particles play two main roles: first role is to prevent bubble polymerization. When CO<sub>2</sub> is introduced into the solution, chaotic circulation occurs, Ca(OH)<sub>2</sub> particles are rapidly shuttled among the CO<sub>2</sub> bubbles and inhibit the bubbles polymerization; second role is to improve the adsorption effect. Ca(OH)<sub>2</sub> particles circulate in the solution with a certain amount of micro CO<sub>2</sub> bubbles adsorbed on their surface, which reduces the amount of bubbles escaping from the liquid surface and increases the residence time.

### 3.2 The Effect of CO<sub>2</sub> Absorption Rate from Pure CO<sub>2</sub>

In order to study the effect of solid particles on ship's decarburization, a contrast experiment is carried out with pure NaOH solution and mixed NaOH solution with CaO solid particles. The concentration of NaOH solution is 1 mol/L, the total volume is 3 L, and CaO's weight is 1.25 g. Figure 3 shows the CO<sub>2</sub> absorption rate varies with time.

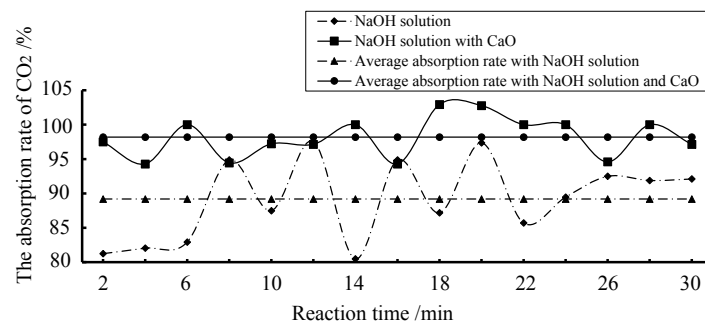


Fig. 3 CO<sub>2</sub> absorption rate varies with time before and after adding CaO particles

It can be seen from Fig. 3 that the average CO<sub>2</sub> absorption rate is 89.2% without CaO and increases by 10% to 98.2% after adding CaO, which means that CaO particulate matters can improve the CO<sub>2</sub> absorption rate significantly. Because CaO is an alkaline substance, after reacting with water, it turns into Ca(OH)<sub>2</sub>, which has a certain chemical absorption to CO<sub>2</sub>, will be generated rapidly. However, the amount of CaO added in this experiment is only 1.25 g, 0.030 7



mol, compared with 3 mol NaOH solution, the difference of alkalinity is nearly 100 times. During the experiment, the average reaction temperature is 27.5°C. The relationship between solubility and the temperature of  $\text{Ca}(\text{OH})_2$  [19] shows that the solubility of  $\text{Ca}(\text{OH})_2$  is 0.156 g at 27.5 °C, so there is only 0.468 g  $\text{Ca}(\text{OH})_2$  dissolved in the mixed solution. From Eq. (3), it can be seen that  $\text{CaCO}_3$  precipitates during the reaction process, and it also participates in the reaction, so the mass of the solid particles changes little during the whole cycle. After adding 1.25 g CaO solid particles, the  $\text{CO}_2$  absorption rate is increased by 10% because of the physical effects.

### 3.3 The Effect of $\text{CO}_2$ Absorption Rate from Simulated Exhaust Gas

Exhaust gas composition of diesel engines is affected by many factors, such as the type of diesel engine, fuel quality, ship operating conditions, etc. Based on the exhaust gas from 6135AZG diesel engine, the representative contents of exhaust gas are selected as  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{SO}_2$  with mass fraction 80.09 %, 15.18%, 4.69% and 0.04% respectively. The simulated exhaust gas is first introduced to the pure NaOH solution, then 1.5 g CaO was added into the NaOH solution with same concentration. Since the acidity of  $\text{SO}_2$  is stronger than  $\text{CO}_2$ , so  $\text{SO}_2$  is assumed to be absorbed completely. Figure 4 shows the absorption rate of  $\text{CO}_2$  contrast.

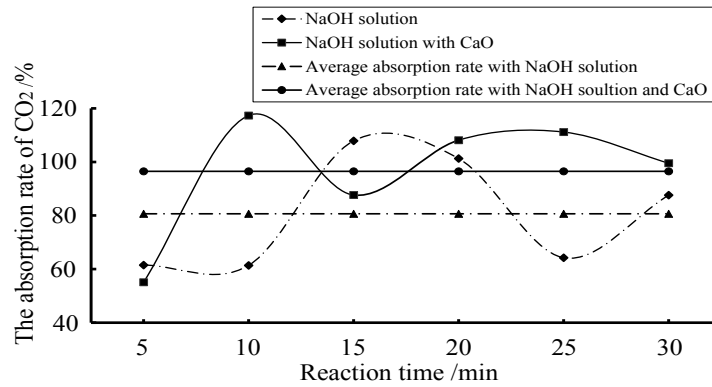


Fig. 4  $\text{CO}_2$  absorption rate varies with time before and after adding CaO to simulated exhaust

We can see that  $\text{CO}_2$  content in the simulated exhaust gas is lower than that of pure  $\text{CO}_2$  gas, so the curve fluctuates wildly but the overall trend of the two absorption curves is about the same, and the main difference is the first half of the reaction, which achieves a better absorption effect due to the presence of solid particles. The average absorption rate of simulated exhaust gas is 80.65% without CaO solid particles and it increases by 15.85% to 96.50% after adding CaO solid particles. It can be seen that neither pure  $\text{CO}_2$  gas, simulated exhaust gas nor CaO solid particulates can improve  $\text{CO}_2$  absorption significantly, and the trend of both charts is very similar.

### 3.4 Experimental with Marine Diesel Engine of 6135AZG

Based on the 6135AZG marine diesel engine, running under load  $L$  characteristics condition at the speed of 1 500  $\text{r}\cdot\text{min}^{-1}$ , the engine operating points and the theoretical displacement are shown in Table 2.

Table 2 Diesel engine load characteristics of 6135AZG

Working condition	Load ratio /%	Fuel consumption / $\text{g}\cdot(\text{kW}\cdot\text{h})^{-1}$	Power /kW	Torque /(N·m)	Theoretical displacement /(m <sup>3</sup> ·h <sup>-1</sup> )	Theoretical displacement of $\text{CO}_2$ /(kg·h <sup>-1</sup> )
1	100%	225.8	162.0	1 031.40	3 414.57	103.84

2	75%	227.0	121.5	773.55	2 814.05	86.89
3	50%	236.0	81.0	515.70	1 950.45	60.24
4	25%	252.0	40.5	257.85	1 040.73	32.12

The exhaust gas outlet temperature is 55 °C after cooling , and other test conditions remain unchanged. Figure 5 shows the test results.

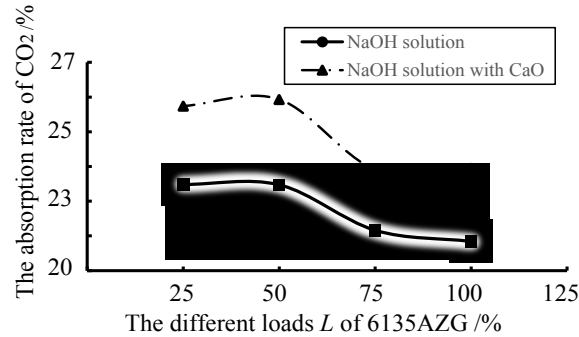


Fig. 5 CO<sub>2</sub> absorption rate varies with time before and after adding CaO to simulated exhaust

From Fig. 5 we can see that when the 6135AZG marine diesel engine runs at 25% load, the exhaust gas CO<sub>2</sub> absorption rate is 22.48% in pure NaOH solution. It falls to 22.47%, 21.16% and 20.84% at 50%, 75% and 100% load respectively. After adding CaO solid particles into the solution, the exhaust gas CO<sub>2</sub> absorption rate rises to 24.74%, 24.93%, 22.92% and 22.95% at 25%, 50%, 75% and 100% load respectively.

### 3.5 The Varies of pH Value on Absorption Solution in Experiment

In the experiment, we find that the pH value obtained by using simulated exhaust of a ship distribution trend is in good agreement with the experiment of 6135AZG marine diesel engine. In other words, the pH value reduction of NaOH solution with CaO solid is slower than the purity NaOH solution, as shown in Fig. 6.

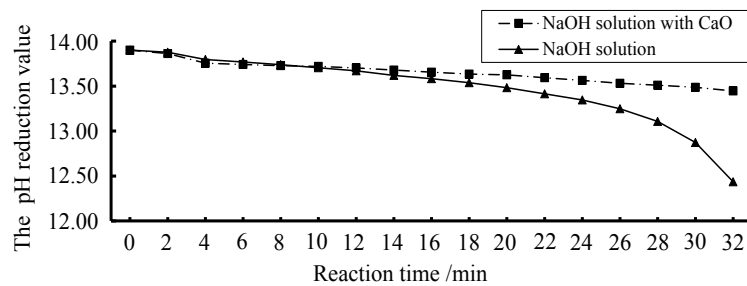


Fig. 6 The pH reduction varies with time using simulated gas and real gas in experiment

At the beginning of the experiment, the pH of NaOH solution with CaO is lower than the purity NaOH solution at 13.88. And the pH values of the two solutions are different in the 14th minute, the pH value of NaOH solution with CaO is 13.70, while the NaOH solution pH value is 13.67.

The pH value of NaOH solution with CaO is 13.56, and the pH value of the purity NaOH solution is 13.35 when the experiment lasts for 24 minutes. The pH value of NaOH solution with CaO is 13.44, the pH of NaOH solution is 12.44 when the experiment lasts for 32 minutes. After the reaction completes, the result shows that the pH value of NaOH solution with CaO decrease by 0.44, while the pH value of the purity NaOH solution is down by 1.46.

### 3.6 The Comparison of CO<sub>2</sub> Absorption Rate in NaOH Solution with and without CaO Particles

When the mole ratio of NaOH to CaO is 135 in the mixed solution. The CO<sub>2</sub> absorption rate reaches to 98.2% to pure CO<sub>2</sub> gas, 10% higher than the pure NaOH solution, the CO<sub>2</sub> absorption rate of the simulated exhaust gas also increases by 15.85% from 80.65% to 96.5%. The CO<sub>2</sub> absorption rate from 6135AZG diesel engine emission also increases by 10.30% from 21.74% to 23.89%, as shown in Fig. 7.

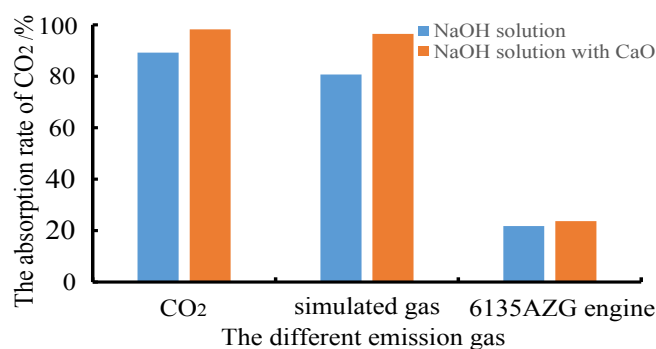


Fig. 7 CO<sub>2</sub> absorption rate varies before and after adding CaO to the different gas

## 4 Conclusion

In this paper, the method of adding CaO solid particles into NaOH solution is proposed to improve CO<sub>2</sub> absorption efficiency. The CaO particles enhancement mechanism is expounded from both chemical and physical aspects. The mathematic enhancement model was derived and the enhancement effect have been verified through the experiment. The experimental result shows that there is a micro bubbles accumulation process during the CO<sub>2</sub> absorption process without adding CaO in the solution and the absorption effect will gradually increase as the micro bubbles form a circulation in the upper part of the reactor, and the average absorption rate can reach the highest level of 89.2%, which is far to achieve the desired value. While, the absorption efficiency improves significantly after adding CaO solid particles. So we can conclude that adding CaO particles into the NaOH solution can improve CO<sub>2</sub> absorption significantly and it has a promising future in the ship exhaust gas handling area.

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